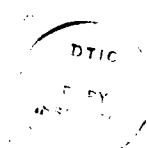


Reactions of *N,N'*-Dimethylurea with Some Boron-Nitrogen Compounds¹

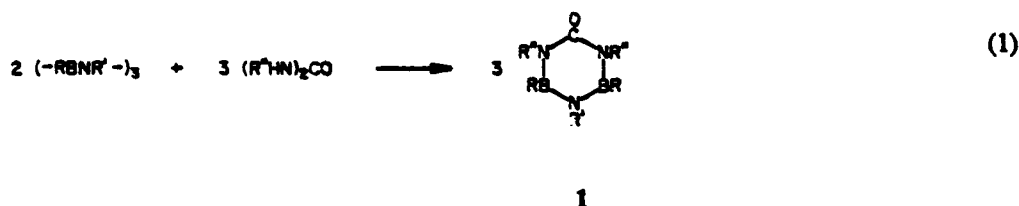
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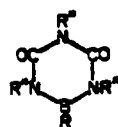


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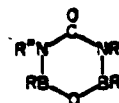
Only two studies on the interaction of boron-nitrogen compounds with ureas are known. Firstly, the reaction of borazines, $(-RBNR')_3$, with urea as well as *N*-mono- and *N,N'*-diorganyl derivatives thereof has been described to proceed according to eq (1). The resultant 1,3,5-triaza-2,6-diboracyclohexane-4-one (= ketotriazadiborinane)



species 1 (obtained in 55 to 65% yield) were characterized by elemental analyses only.² Several compounds



2



3

containing the same structural skeleton of 1 and related species such as 2 and 3 were found among the reaction products of (halo)organylboranes with *N*-organosubstituted ureas as well as *N*-lithiated³ or *N*-silylated^{4,5} derivatives of the latter.

In another study, equimolar amounts of *N,N'*-dimethylurea, $(R''HN)_2CO$ ($R'' = CH_3$), and tris(dialkylamino)boranes, $B(NR'_2)_3$ ($R' = CH_3, C_2H_5$), were found to react in boiling xylene to give good yields of 1,5-diaza-2,4-dibora-3-oxacyclohexan-6-ones, 3.⁴

The present work is concerned with a study of the reaction of *N,N'*-dimethylurea with various types of boron-nitrogen compounds containing trigonal boron.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded for solutions in $CDCl_3$ (unless otherwise noted) on a Varian XL-200 or VXR-400 (^{11}B) or GEMINI-200 (1H , ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal $(CH_3)_4Si$ for 1H and ^{13}C NMR, external $(C_2H_5)_2O-BF_3$ for ^{11}B NMR). Abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet. An asterisk denotes a broad signal. Coupling constants J are given in hertz. All ^{13}C NMR spectra were recorded in the proton decoupled mode. Mass spectral data (70 eV unless otherwise noted) were recorded on a VG ZAB-2F spectrometer; data are given to m/z 30 for 5% or greater relative abundances (in parentheses) only.

$C_2H_5B(\mu-NH)(\mu-NCH_2CONCH_3)BC_2H_5$ (1a; $R = C_2H_5$, $R' = H$, $R'' = CH_3$). A mixture of 11.7 g (71 mmol) of *B*-triethylborazine, $(-C_2H_5BNH-)_3$,⁶ and 9.4 g (107 mmol) of *N,N'*-dimethylurea was heated in an oil-bath of 200 °C for 6 h. After cooling to room temperature, the material solidified. It was extracted with several portions of ether to leave a polymer-like brown residue (which was not further investigated). The ether was evaporated from the clear solution and the colorless solid residue was recrystallized from pentane to give 9.4 g (48%) of product, mp 95-98 °C. Anal. Calcd for $C_7H_{17}B_2N_3O$ ($M_r = 180.85$): C, 46.48; H, 9.47; B, 11.95; N, 23.23; O, 8.85. Found: C, 46.35; H, 9.45; B, 9.73; N, 22.98.

NMR data: δ (1H) 5.25* (1 H, s), 3.01 (6 H, s), 1.02 (10 H, s); δ (^{11}B) 36.2 ($h_{1/2} = 265$ Hz); δ (^{13}C) 160.0, 30.8, 8.0, 7.5*. Mass spectrum: m/z 181 (49), 180 (100), 179 (41), 178 (6), 153 (6), 152 (11), 151 (5), 123 (13), 122 (6), 95 (7), 94 (5), 68 (5), 67 (7), 66 (9), 40 (7), 38 (5).

$C_2H_5B(\mu-NCH_3)(\mu-NCH_3CONCH_3)BC_2H_5$ (1b; $R = C_2H_5$, $R' = R'' = CH_3$) was prepared in analogous fashion as the preceding compound by reaction of 5.5 g (27 mmol) of *B*-triethyl-*N*-trimethylborazine, $(-C_2H_5BNCH_3-)_3$,⁶ with 3.5 g (40 mmol) of *N,N'*-dimethylurea (5 h at 180 °C bath temperature). The resultant product was distilled under vacuum to give 5.4 g (70%) of the desired product, bp 115 °C/1 torr. Anal. Calcd for $C_8H_{19}B_2N_3O$ ($M_r = 194.88$): C, 49.31; H, 9.83; B, 11.09; N, 21.56; O, 8.21. Found: C, 49.06; H, 9.87; B, 10.82; N, 21.43.

NMR data: δ (1H) 3.11 (6 H, s), 2.99 (3 H, s), 1.2 to 0.9 (10 H, m); δ (^{11}B) 36.7 (s, $k_{1/2} = 280$ Hz); δ (^{13}C) 159.0, 32.2, 31.2, 6.5*. Mass spectrum: m/z 196 (14), 195 (60), 194 (100), 193 (36), 192 (17), 181 (5), 168 (10), 167 (13), 166 (16), 165 (15), 137 (16), 136 (8), 125 (6), 109 (14), 108 (5), 81 (9), 80 (10), 68 (9), 66 (5), 52 (8), 51 (6), 44 (10), 40 (16), 32 (22).

$CH_3N(\mu-BC_6H_5)(\mu-CONCH_3CO)NCH_3$ (2; $R = C_6H_5$, $R' = R'' = CH_3$). A mixture of 1.0 g (2.8 mmol) of *B*-triphenyl-*N*-trimethylborazine, $(-C_6H_5BNCH_3-)_3$,⁶ and 2.0 g (22.7 mmol) of *N,N'*-dimethylurea was carefully molten and then boiled for 10 min. After cooling to room temperature, 200 mL of benzene was added and the mixture was refluxed with stirring for 15 min. The clear solution was decanted from a small amount of insoluble material and benzene was evaporated. Unreacted urea was sublimed off under vacuum (80 °C bath temperature). The residue was dissolved in 50 mL of benzene, insoluble material was discarded, and benzene was evaporated. The remaining solid was sublimed under vacuum to give 1.6 g (62%) of product, mp 126-128 °C, identical (NMR) with the previously described material⁷ (obtained from the $[(CH_3)_2N]_2BC_6H_5$ with *N,N',N''*-trimethylbiuret).

$CH_3B[\mu-N(CH_3)_2][\mu-NCH_3CONCH_3][\mu-NCH_3CONHCH_3]BCH_3$ (4a). A mixture of 1 g (11.4 mmol) of *N,N'*-dimethylurea, 2 g (17.6 mmol) of bis(dimethylamino)methylborane, $[(CH_3)_2N]_2BCH_3$,⁸ and 100 mL of toluene was refluxed with stirring for 9 h. Toluene was evaporated from the clear solution under reduced pressure. The solid residue (0.9 g, 59%) was recrystallized from acetonitrile to give a colorless product, mp 240-242 °C. Anal. Calcd for $C_{10}H_{23}B_2N_5O_2$ ($M_r = 268.93$): C, 44.66; H, 9.37; B, 8.04; N, 26.03; O, 11.90. Found: C, 44.73; H, 9.57; B, 7.97; N, 25.94.

NMR data: δ (1H) 4.9* (1 H, s), 2.81 (6 H, two closely spaced d), 2.71 (3 H, s), 2.59 (3 H, s), 2.15 (3 H, s), 2.11 (3 H, s), -0.06 (3 H, s), -0.07 (3 H, s); δ (^{13}C) 162.1, 158.9, 40.0, 31.8, 31.6, 31.0, 27.6, -0.6* (ratio for 162.1

and 158.9 signal ca. 1:2). Major ion peaks appear in the mass spectrum of the compound in the regions near m/z 269, 197, 168, and 125.

$C_{12}H_{29}B[\mu-N(CH_3)_2][\mu-NCH_3CONCH_3][\mu-NCH_3CONHCH_3]BC_2H_5$ (4b). A solution of 11.6 g (91 mmol) of bis(dimethylamino)ethylborane, $[(CH_3)_2N]_2BC_2H_5$,⁸ in 50 mL of toluene was added dropwise with stirring to a hot solution of 4.0 g (45.5 mmol) of *N,N'*-dimethylurea in 100 mL of toluene. The mixture was refluxed overnight and the solvent was evaporated under reduced pressure. The colorless residue was washed with pentane and then with ether to give 4.8 g (71%) of crude product, mp 226–228 °C (after recrystallization from acetonitrile). Anal. Calcd for $C_{12}H_{29}B_2N_5O_2$ ($M_r = 296.98$): C, 48.53; H, 9.84; B, 7.28; N, 23.57; O, 10.78. Found: C, 48.39; H, 10.12; B, 6.58; N, 24.35.

NMR data: δ (1H) 6.2* (1 H, s), 2.85 + 2.81 (6 H, two closely spaced d), 2.69 (3 H, s), 2.58 (3H, s), 2.24 (3 H, s), 2.16 (3 H, s), 0.91 (6 H, q, $J = 7.5$), 0.68 (2 H, t, $J = 7.5$), 0.55 (2 H, t, $J = 7.5$) (the positions of the signals at 6.2 (up to 0.5 ppm) and 2.8 ppm (very slightly) are concentration-dependent); δ (^{11}B) 1.3 (s, $h_{1/2} = 635$ Hz); δ (^{13}C) 163.6, 159.9, 40.3, 40.0, 31.6, 31.3, 30.8, 27.5, 10.3, 9.8, 6.9*. The mass spectrum exhibits a weak parent ion cluster in the region m/z 297; the base peak is observed at m/z 211.

$C_6H_6B[\mu-N(CH_3)_2][\mu-NCH_3CONCH_3][\mu-NCH_3CONHCH_3]BC_6H_5$ (4c). A mixture of 3.0 g (17.1 mmol) of bis(dimethylamino)phenylborane, $[(CH_3)_2N]_2BC_6H_5$,⁹ 1.0 g (11.4 mmol) of *N,N'*-dimethylurea, and 80 mL of toluene was refluxed with stirring for 10 h. The colorless precipitate was collected, washed with pentane, and dried under vacuum to give 1.7 g (75% yield) of product A (= 4c), mp 284–286 °C. Anal. Calcd for $C_{20}H_{29}B_2N_5O_2$ ($M_r = 393.10$): C, 61.11; H, 7.44; B, 5.50; N, 17.81; O, 8.14. Found: C, 60.06; H, 7.54; B, 5.40; N, 18.29. This material was readily soluble in chloroform (up to 3.7 wt%) and NMR spectra were recorded.

NMR data: δ (1H) 7.7 + 7.4 + 7.3 (10 H, unresolved m), 6.9* (1 H, s), 3.02 (3 H, d, $J = 4.4$), 3.00 (3 H, s), 2.84 (3 H, s), 2.64 (3 H, s), 2.20 (3 H, s), 1.68 (3 H, s); δ (^{11}B) 3.2 (s, $h_{1/2} = 250$ Hz); δ (^{13}C) 165.1, 161.5, 135.8, 134.9, 133.9, 127.3, 127.2, 127.0, 126.9, 41.4, 40.8, 34.4, 34.0, 33.7, 28.0. The mass spectrum exhibits a strong parent ion cluster in the region m/z 392.

The material A was recrystallized from chloroform/cyclohexane (1:1 by volume) to give a product analyzing as a 1:1 molar adduct of 4c with chloroform, mp 278–280 °C. Anal. Calcd for $C_{21}H_{30}B_2Cl_2N_5O_2$ ($M_r = 512.55$): C, 49.21; H, 5.90; B, 4.22; Cl, 20.75; N, 13.66; O, 6.26. Found: C, 49.06; H, 6.08; B, 3.81; Cl, 19.57; N, 14.21.

This latter material B was considerably less soluble in chloroform (only up to 1.8 wt%) than the original material 4c. However, the ^1H NMR spectrum was essentially identical with that of 4c except that the signal of 4c observed at 6.4 ppm is now located at 5.3* ppm (1 H) and an additional signal is observed at 1.43 ppm (1 H, s, position concentration dependent). An additional signal was also observed in the ^{13}C NMR spectrum (solution in CD_2Cl_2) at 78.0 ppm.

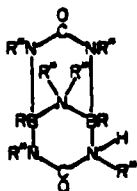
Reaction of *N,N'*-Dimethylurea with (Dimethylamino)diorganylboranes (Representative Reaction). A mixture of 6.0 g (42.5 mmol) of (dimethylamino)di-*n*-propylborane, $(\text{CH}_3)_2\text{NB}(\text{n-C}_3\text{H}_7)_2$ ¹⁰ and 1.0 g (11.4 mmol) of *N,N'*-dimethylurea was heated to reflux (190 °C bath temperature) with stirring. After about 1 h a clear homogeneous mixture was obtained and heating was continued for 45 h. A colorless precipitate formed on cooling of the reaction mixture to room temperature and additional precipitate formed on addition of 40 mL of pentane. The precipitate was collected and was identified as *N,N,N'*-trimethylurea (78% yield); δ (^1H) 4.4* (1 H, s), 2.89 (6 H, s), 2.79 (3 H, d, $J = 4.7$). Pentane was distilled off the filtrate under reduced pressure and the remaining liquid was fractionally distilled under vacuum to yield $(\text{CH}_3)\text{HNB}(\text{n-C}_3\text{H}_7)_2$ and the unreacted excess of $(\text{CH}_3)_2\text{NB}(\text{n-C}_3\text{H}_7)_2$.

Results

The reaction of *N,N'*-dimethylurea (= DMU) with borazines according to eq (1) has previously been reported in a patent,² but no experimental details are available. It has now been observed that no reaction occurred when several borazines, $(-\text{RBNR}'-)_3$ ($\text{R} = \text{C}_2\text{H}_5$ or C_6H_5 and $\text{R}' = \text{H}$ or CH_3), were treated with the urea in heat transfer media such as refluxing benzene, toluene, or xylene. However, heating of a neat mixture of the reactants to temperatures of 180-200 °C gave ready access to 1a ($\text{R} = \text{C}_2\text{H}_5$, $\text{R}' = \text{H}$, $\text{R}'' = \text{CH}_3$) and 1b ($\text{R} = \text{C}_2\text{H}_5$, $\text{R}' = \text{R}'' = \text{CH}_3$) originating from $(-\text{C}_2\text{H}_5\text{BNR}'-)_3$ with $\text{R}' = \text{H}$ or CH_3 , respectively. When $(-\text{C}_6\text{H}_5\text{BNCH}_3-)_3$ was heated with DMU to 200 °C, the mixture was not yet completely liquefied. Only at bath temperatures near 250 °C (boiling DMU) was a clear melt obtained and a reaction initiated. However, the resultant product consisted primarily of 1,3,5-triaza-2-boracyclohexan-4,6-dione 2 with $\text{R} = \text{C}_6\text{H}_5$ and $\text{R}' = \text{CH}_3$. This result suggests that under the experimental conditions a condensation of the DMU to *N,N,N'*-trimethylbiuret occurred first, and the latter reacted with the borazine to give the cited product. Compounds of type 2 have previously been obtained by transamination

of bis(dimethylamino)organylboranes with biurets,⁷ and were also observed among the products of the condensation of (dihalo)organylboranes with ureas.³

In the present work it also further found, that bis(dimethylamino)organylboranes, $[(CH_3)_2N]_2BR$, react with DMU in 1:1 molar ratio and with the release of only 1.5 equiv of dimethylamine to form diboron species. The process is independent of the ratio of the reactants. However, the products are most easily purified when an excess of the aminoborane is used. (No bis(ureido)boranes of the type $RB(NR'CONHR')_2$ could be obtained under the studied conditions, not even in the presence of a large excess of the urea.) The resultant diboron species unexpectedly contained four-coordinate boron (as shown by ^{11}B NMR data), suggesting 4 as the structure of the



4 $(R'' = CH_3)$

a: $R = CH_3$

b: $R = C_2H_5$

c: $R = C_6H_5$

species. This latter formulation is in complete consonance with all of the NMR data.

When a neat mixture of (dimethylamino)di-n-propylborane and DMU was refluxed (for 1-2 d) using excess of the aminoborane as solvent, essentially quantitative conversion of the DMU to *N, N, N'*-trimethylurea (= TMU) was observed besides the formation of (methylamino)di-n-propylborane. (Dimethylamino)diethylborane¹¹ did not react with DMU under analogous conditions (ca. 125 °C). However, using boiling xylene as solvent (ca. 140 °C) a reaction occurred which resulted again in an essentially quantitative conversion of the DMU to TMU and of the (dimethylamino)diethylborane to (methylamino)diethylborane within a period of 1 d. On refluxing of (the higher boiling) (dimethylamino)diphenylborane with DMU, a reaction occurred within a period of 15 h to again yield TMU and (methylamino)diphenylborane.

These observations illustrate that displacement of the dimethylamino groups of (dimethylamino)diorganylboranes by DMU in a transamination reaction does not occur readily. Rather, under the conditions used the DMU appears to decompose to methyl isocyanate and methylamine. Subsequently, methylamine exchanges place with the dimethylamino group of the borane, and the generated dimethylamine interacts with the isocyanate to yield TMU. Indeed, an intermediate decomposition of *N,N'*-diorganylureas in the reaction with haloboranes has been noted earlier,³ and displacement of dialkylamino groups of (dialkylamino)diorganylboranes by methylamine has been described as an exothermic reaction.¹²

In contrast, equimolar amounts of tris(dialkylamino)boranes, $B(NR'_2)_3$ ($R' = CH_3, C_2H_5$), and DMU have been reported to react in boiling xylene to give species of type 3 (with $R = NR'_2$ where $R' = CH_3$ or C_2H_5).⁴ Apparently, this latter reaction proceeds via the intermediate formation of the carbodiimide $CH_3N=C=NCH_3$ and the diboroxane (= diboryl oxide) $[(R'_2N)_2B]_2O$ (under release of two molar equiv of R'_2NH); the diboroxane then seems to react with a second DMU molecule in a transamination to yield a cyclic product of type 3. In view of the observation that aminoboranes tended to react with DMU to form at least one $BNCH_2CONCH_2B$ unit, tris(dimethylamino)borane¹³ was reacted with DMU in 2:3 molar ratio in refluxing toluene (24 h). A glassy polymer-like material was obtained, the ¹¹B NMR spectrum of which showed at least four distinct resonance signals centered near 0 ppm (maxima at 2.4, -0.1, -1.0, and -1.4 ppm). The ¹H NMR spectrum of this product was inconclusive, and the 70 eV mass spectrum exhibited peaks up to *m/z* 572. This material was not further investigated.

Acknowledgment. This work was supported by the Office of Naval Research (K.N.).

Footnotes and References

† On leave of absence from the Technical University of Wrocław, Poland.

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